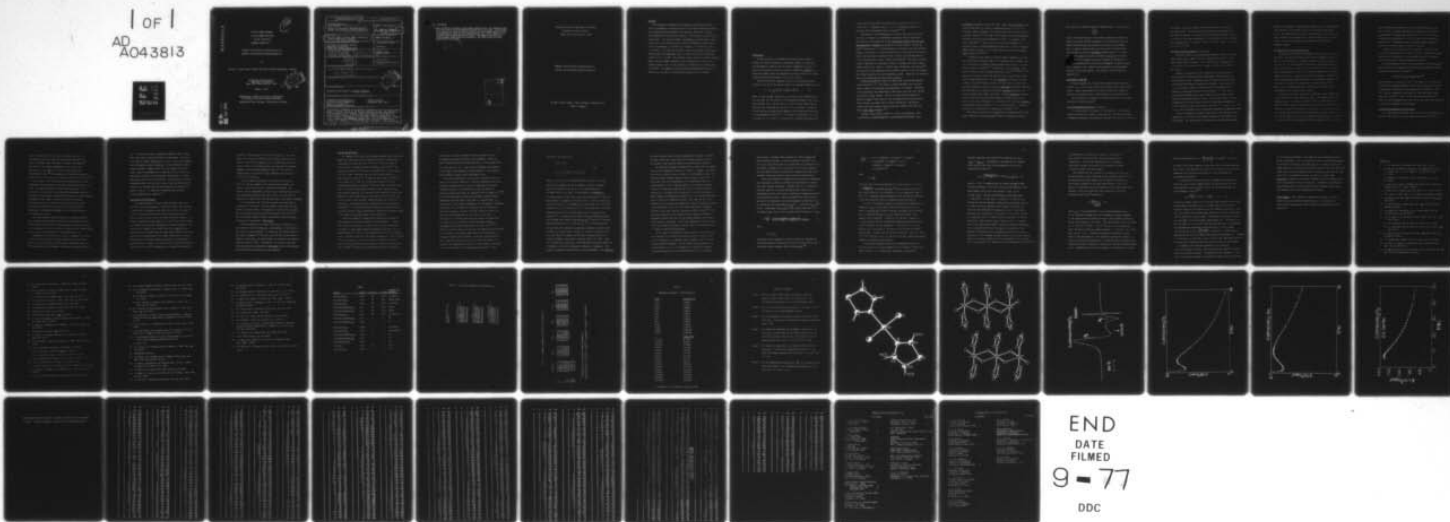


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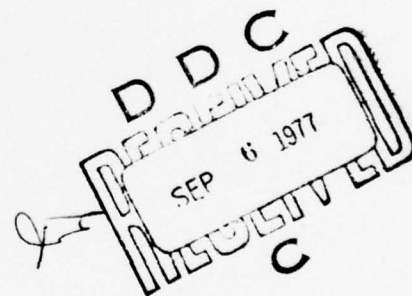
Magnetic and Structural Characterization of
Dibromo- and Dichlorobis(thiazole)copper(II)

by

William E. Estes, Diane P. Gavel, William E. Hatfield and Derek J. Hodgson

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Chapel Hill, North Carolina 27514

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Magnetic and Structural Characterization of
Dibromo- and Dichlorobis(thiazole)copper(II)

William E. Estes, Diane P. Gavel, William E. Hatfield*, and
Derek J. Hodgson*

ABSTRACT

The temperature dependence of the magnetic susceptibility and the electron paramagnetic resonance spectra of the thiazole complexes dichloro- and dibromobis(thiazole)copper(II) are reported, along with a complete three-dimensional X-ray structure analysis of the dichloro complex based on counter data. The dichloro complex, $\text{Cu}(\text{C}_3\text{H}_3\text{NS})_2\text{Cl}_2$, crystallizes in space group $\text{P2}_1/\text{c}$ of the monoclinic system with two independent formula units in a cell of dimensions $\underline{a} = 7.332(6)$, $\underline{b} = 3.853(4)$, $\underline{c} = 17.493(17)$ Å, and $\beta = 93.70(1)^\circ$. The structure has been refined by full-matrix least-squares methods using 1172 independent data to a final value of the conventional R-factor (on F) of 0.028. The structure, which consists of infinite chains of doubly chloride bridged copper(II) ions, is reminiscent of those of the pyridine analogs, with a Cu-Cu separation of $3.853(4)$ Å and bridging angle of $91.89(2)^\circ$. The magnetic data and interchain exchange interactions are discussed in the light of the structural properties of the systems.

INTRODUCTION

Current interest in one-dimensional exchange-coupled magnetic systems has recently stimulated a considerable number of theoretical and experimental studies as well as several comprehensive reviews.¹⁻⁵ Most of the theoretical work has centered on completely isolated one-dimensional models, while the experimental work has reflected the longer range interactions which always occur in real crystals.

From the theoretical standpoint, most of the investigations have centered on the use of the various forms of the spin-spin Hamiltonian (1)

$$H = -2J \sum_{i < j} [a \hat{S}_z^i \cdot \hat{S}_z^j + b(\hat{S}_x^i \cdot \hat{S}_x^j + \hat{S}_y^i \cdot \hat{S}_y^j)] \quad (1)$$

where J is the exchange integral, S_x , S_y , and S_z are the components of the total spin (S), the ratio a/b is an anisotropy parameter, and i and j label adjacent ions. For the case $a = 1$ and $b = 0$, the Ising model is obtained; and, in the special case for $S = 1/2$, an "exact" closed-form solution has been obtained for the magnetic and thermodynamic properties of a one-dimensional chain.^{4,5,6} If the spins are restricted to lie in x - y plane, i.e. $a = 0$ and $b = 1$, then the X - Y or planar Heisenberg model

is obtained; and, Katsura⁷ has obtained exact solutions for the $S = 1/2$ linear chain. Furthermore, when $a = b = 1$, the exchange interaction is isotropic and the Heisenberg model is obtained.^{8,9,10}

Unfortunately, in the Heisenberg or isotropic limit, no closed form solutions for magnetic or thermodynamic properties have yet been found; this being the case, almost all of the theoretical analyses have used some approximations to estimate the properties of linear chains.⁹ Bonner and Fisher⁸ studied the $S = 1/2$ antiferromagnetic Heisenberg chain and performed computer calculations on finite rings and chains of isotropically interacting spins; they were able to estimate rather accurately the limiting behavior of the infinite linear system. Katsura and coworkers¹¹ have applied "linked-cluster" expansions via perturbation theory to estimate the various thermodynamic functions of interest. Finally, Baker, Rushebrooke and coworkers^{9,10} have employed a high temperature series expansion method to study the magnetic and thermal properties of linear Heisenberg systems. Generally, the results of Bonner and Fisher have been most widely accepted.¹

Numerous experimental studies of linear chain crystals have appeared in the literature.^{1-3,5} The results of these experiments have been analyzed in terms of the available one-dimensional (1-D) models. Transitions to the long-range, three-dimensional ordered state have also been observed for several of these systems. Since it is known from the theorems of Mermin and Wagner¹² that pure one- and two-dimensional isotropic systems cannot sustain long range order at finite temperatures, considerable interest has been focused on linear Heisenberg complexes with small but finite inter-chain exchange.^{13,14}

Perhaps the most famous example of a nearly one-dimensional chain is provided by tetramethylammonium trichloromanganate(II) (TMMC), whose

intra-chain exchange is about 9 cm^{-1} with longer range inter-chain interactions being about four orders of magnitude smaller.¹⁶ For $S = 1/2$ complexes, copper tetraamine sulfate monohydrate (CTS) has been the most thoroughly studied,¹⁷⁻²¹ but some recently reported electron paramagnetic resonance results have been interpreted in terms of a quadratic rather than linear model.²² Finally, one of the best known examples of a $S = 1/2$ Heisenberg chain is dichlorobis(pyridine)copper(II), in which the intra-chain exchange is about 9 cm^{-1} is much larger than the observed inter-chain coupling.^{13-15,23,24}

A relatively large number of transition metal complexes of the general stoichiometry $M(\text{II})L_2X_2$ (where M is a divalent first row metal ion, L is a heterocyclic nitrogen containing organic base, and $X = \text{Cl}$ or Br) has been shown to contain,^{24,27} or behave as if they contained, linear magnetic chains of doubly halogen-bridged metal ions.^{13-15,28,29a,23,33,34} Typically, structural studies have shown that the $M L_2 X_2$ systems contain doubly halogen bridged metal ions with intrachain metal-metal distances of about 4 \AA and $M-X-M$ angles of about 90° (See Table 1); these chains are usually packed in such a way that the interchain metal-metal distances are much longer (i.e. greater than 8 \AA) than intrachain distances, and pseudo-one-dimensional chains are formed. Although interchain distances seem to imply quite weak interchain magnetic exchange, these effects have been observed; furthermore, it is believed that these weak interchain superexchange pathways involve $M - X \cdots N - M$ interactions. A thorough discussion of the properties of $\text{Cu}(\text{py})_2\text{Cl}_2$ is available.^{13,14}

With these facts in mind, the bis(thiazole) dihalogen metal(II) complexes reported by Underhill, *et al.*³⁰ became of considerable interest.

The structure of thiazole (C_3H_3NS) is depicted below. Since the elec-



tronic and infrared spectra of the thiazole complexes were similar to those of the known pyridine analogues, it was proposed that the compounds $Cu(thiazole)_2X_2$ were polymeric with double halide bridges. Also, it might be expected that the sulfur atom of the heterocycle could provide an efficient interchain exchange pathway. In order to confirm the original postulates of Underhill, et al., and to examine possibility of enhanced interchain exchange, we undertook low temperature susceptibility and electron paramagnetic resonance studies of the complexes, and a complete three-dimensional crystallographic analysis of the chloro complex. The results of these studies are reported here.

EXPERIMENTAL PROCEDURE

Thiazole (C_3H_3NS , Tz), obtained from Columbia Organic Chemicals, Columbia, S.C., was of *puriss* grade and was used without further purification. Reagent grade copper(II) chloride dihydrate and copper(II) bromide were obtained from J.T. Baker Chemical Co. and used directly.

Both complexes were prepared by a slight modification of the method described by Underhill et al.³⁰

Dichlorobis(thiazole)copper(II), $Cu(tz)_2Cl_2$

To a warm solution of thiazole (0.51 g, 6mmol) in ~1 ml absolute ethanol was added 0.5g, (3mmol) of $CuCl_2 \cdot 2H_2O$ in ~8 ml absolute ethanol. An immediate turquoise blue precipitate resulted; the mixture was stirred for

ten minutes, collected, washed with ether and benzene, and allowed to dry under suction. The product was recrystallized from dimethylformamide (DMF) by addition of an equal volume of methylene chloride followed by cooling in the freezer compartment of a refrigerator. Anal: Calculated for $\text{Cu}(\text{C}_6\text{H}_6\text{N}_2\text{S}_2)\text{Cl}_2$: C = 23.65, H = 1.98, Cl = 23.27. Found: C = 23.56, H = 2.08, Cl = 23.51.

Dibromobis(thiazole)copper(II), $\text{Cu}(\text{tz})_2\text{Br}_2$

$\text{Cu}(\text{tz})_2\text{Br}_2$ (hitherto not reported) was prepared as above. The dark green powder ($\bar{\nu}_{\text{max}} = 14285 \text{ cm}^{-1}$) was recrystallized as above to yield darker green hair-like needles. Anal. Calculated for $\text{Cu}(\text{C}_6\text{H}_6\text{N}_2\text{S}_2)\text{Br}_2$: C = 18.31, H = 1.55, and Br = 40.6. Found: C = 18.31, H = 1.62 and Br = 40.42.

Magnetic susceptibilities were obtained on a Princeton Applied Research model 155 vibrating sample magnetometer (VSM) operating at a field strength of 10kG. Temperatures at the sample were measured with a calibrated GaAs diode by observing the voltage on a Dana model 4700 4.5 place digital voltmeter; further details of the apparatus and temperature measurement have been given elsewhere.³¹ Finely-ground polycrystalline samples which were enclosed in Lucite sample holders typically weighed approximately 150 mg. The data were corrected for the diamagnetism of the Lucite holder and for the underlying diamagnetism of the constituent atoms using Pascal's constants.³² A value of 60×10^{-6} c.g.s. units was assumed for the temperature independent paramagnetism (TIP).

Electron paramagnetic resonance (epr) spectra were obtained at room temperature on a Varian E-3 spectrometer operating at approximately 9.5 GHz (X-Band). All spectra were recorded from very finely ground powders

enclosed in commercially available quartz sample tubes. Several spectra were recorded at 77°K through the use of an insertion Dewar made by Varian. The magnetic field of the E-3 was calibrated by nmr techniques using a Magnion G-502 gaussmeter and a Hewlett-Packard 5340A frequency counter. The klystron frequency was observed directly with the frequency counter.

Determination of the Crystal Structure

Weissenberg and precession photographs indicated that the crystals belonged to the monoclinic system, the observed systematic absences of $0k0$ for k odd and $h0l$ for l odd being consistent only with the space group $P2_1/c$. The cell constants, determined by least-squares methods, are $a = 7.332$ (6), $b = 3.853$ (4), $c = 17.493$ (17) Å and $\beta = 93.7$ (1)°; these observations were made at 21°C with $\text{MoK}\alpha$ radiation with λ ($\text{MoK}\alpha$) assumed as 0.7093 Å. A density of 2.03 g cm^{-3} obtained by flotation in carbon tetrachloride/bromoform mixtures is in acceptable agreement with the value of 2.05 g cm^{-3} calculated for two formula units per cell. Hence, in the centrosymmetric space group $P2_1/c$, the copper atom is constrained to lie on the inversion center.

Diffraction data were collected on a platelike crystal having faces (102) , $(\bar{1}0\bar{2})$, (001) , $(00\bar{1})$, (010) , and $(0\bar{1}0)$. The separations between opposite pairs of faces were as follows: (102) to $(\bar{1}0\bar{2})$, 0.0056 cm; (001) to $(00\bar{1})$, 0.014 cm; and (010) to $(0\bar{1}0)$, 0.061 cm. The crystal was mounted on a glass fiber parallel to the b -axis, and data were collected on a Picker four-circle automatic diffractometer using $\text{MoK}\alpha$ radiation. The take off angle was 1.5°; at this angle the peak intensity of a typical strong reflection was approximately 95% of its maximum value. A total of

1761 reflections was examined by the θ - 2θ scan technique at a scan rate of $1^\circ/\text{min}$. Allowance was made for the presence of both $K\alpha_1$ and $K\alpha_2$ radiations, the peaks being scanned from -1.0° in 2θ below the calculated $K\alpha_1$ peak position to $+1.0^\circ$ in 2θ above the calculated $K\alpha_2$ peak position. Stationary-counter, stationary-crystal background counts of 20 sec were taken at each end of the scan.

A unique data set having $2\theta < 60^\circ$ was gathered. There were few reflections above background at values of $2\theta > 60^\circ$. Throughout the data collection, the intensities of three standard reflections, measured every 100 reflections, remained essentially constant.

Data processing was carried out as described by Corfield, *et al.*³⁶ After correction for background the intensities were assigned standard deviations according to the formula³⁶

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{1/2}$$

with the value of p chosen to be 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz-polarization effects and for absorption factors. The absorption coefficient for the sample with Mo radiation is 31.25 cm^{-1} , and the transmission coefficients for the data crystal range from 0.56 to 0.87.³⁷ A total of 1761 reflections was collected, of which 1172 were independent data with $I > 3\sigma(I)$; only these data were used in the final refinement of the structure.

Solution and Refinement of the Structure

All least-squares refinement were carried out on F minimizing the function $\sum w(|F_o| - |F_c|)^2$, with the weights w defined as $4F_o/\sigma^2(F_o^2)$.

In all calculations of F_c the atomic scattering factors for all non-hydrogen atoms were taken from International Tables^{38a} and those for hydrogen taken from Stewart, Davidson, and Simpson.³⁹ The effects of the anomalous dispersion of Cu, S and Cl were included in F_c , the values of $\Delta f'$ and $\Delta f''$ being taken from International Tables.^{38b} The unweighted and weighted residuals are defined as $R_1 = \sum (|F_o| - |F_c|) / |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.

The location of the chlorine atom was determined from a three-dimensional Patterson function, the copper atom being assigned to the origin. Isotropic refinement of these positions gave $R_1 = 0.476$, $R_2 = 0.540$. The positions of the remaining non-hydrogen atoms were determined from subsequent difference Fourier maps, and a least-squares refinement in which copper, chlorine and sulfur were refined anisotropically while the nitrogen and carbon atoms were refined isotropically yielded values of R_1 and R_2 of 0.045 and 0.063, respectively. Anisotropic refinement of all of these atoms gave $R_1 = 0.034$ and $R_2 = 0.051$.

The three hydrogen atoms were located in a difference Fourier map; a least-squares refinement in which the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically converged to values of R_1 and R_2 of 0.028 and 0.036, respectively, with the error in an observation of unit weight being 1.41.

Examination of the values of $|F_c|$ and $|F_o|$ suggested to us that no correction for secondary extinction is necessary, and none was applied. In the final cycle of least-squares refinement, there were 1172 observations and 73 variables, a reflection to variable ratio of

16:1. In this final cycle, no parameter underwent a shift of more than 0.136, which is taken as evidence of convergence. The value of R_2 shows no unusual dependence on $|F_o|$ or on $\sin\theta$, which suggests that our weighting scheme is adequate. A final difference Fourier showed two peak of height 0.67 eA^{-3} near the copper and chlorine atoms. Which are presumably due to some small error in either our absorption correction or the anisotropic thermal model. No other peak higher than 0.58 eA^{-3} was observed. The positional and thermal parameters derived from this final cycle, along with their standard deviations as estimated from the inverse matrix, are presented in Tables II and III. A compilation of observed and calculated structure amplitudes is available.⁴⁰

Description of the Structure

The complex consists of square planar $\text{Cu}(\text{tz})_2\text{Cl}_2$ units which are linked by chloride bridges to form linear chains. The structure of each chain is, therefore, quite similar to that of $\text{Cu}(\text{py})_2\text{Cl}_2$.²⁴ A view of the square planar array around a single copper ion is shown in figure 1, and a view of the chain is given in figure 2. The overall coordination around copper is, as can be seen in this figure, the commonly-occurring (4+2) tetragonally elongated octahedral. The base plane is formed by the nitrogen atoms of two trans-thiazole groups and by two chloride ions, the axial ligands being chloride ions which are in the base planes of the copper centers above and below. The base plane is strictly planar, there being a crystallographic inversion center at copper. The Cu-N and Cu-Cl (in-plane) distances of 1.990 (2) and 2.322 (1) Å, respectively, are normal and comparable to

values²⁴ of 2.004 (2) and 2.299 (2) Å in $\text{Cu}(\text{py})_2\text{Cl}_2$. The out-of-plane Cu-Cl' distance of 2.998 (1) Å is slightly shorter than the value of 3.026 (2) Å in $\text{Cu}(\text{py})_2\text{Cl}_2$, but is comfortably within the range of 2.698 to 3.37 Å reported for such distances in tetragonal pyramidal dichloro-bridged copper(II) dimers.⁴¹ The Cu-Cl-Cu' bridging angle of 91.89 (2)° is again comparable to the value of 91.52 (5)° in $\text{Cu}(\text{py})_2\text{Cl}_2$.

The bond lengths and angles in the molecule are listed in Table IV. The bond lengths in the thiazole moiety appear to be typical of those found in other conjugated ring systems. The thiazole ring is approximately planar, with no atom deviating from the best least-squares plane by more than 0.006 Å. The ring plane is inclined at an angle of 60° from the base plane of the copper octahedron.

It is noteworthy that the sulfur atom does not participate in coordination to the metal. The only possible interaction involving sulfur is an inter-chain S...S separation of 3.619 (1) Å; this value, which is slightly less than twice the reported⁴² value (1.85 Å) of the van der Waals radius of sulfur, may indicate a weak inter-chain interaction in the crystals (vide infra).

While the geometry at any given copper atom in $\text{Cu}(\text{tz})_2\text{Cl}_2$ is very similar to that in $\text{Cu}(\text{py})_2\text{Cl}_2$, the arrangement of the chains in the crystal is quite different. In $\text{Cu}(\text{py})_2\text{Cl}_2$ the "square planes" in each chain are parallel,²⁴ but this is not the case in the thiazole complex; in $\text{Cu}(\text{tz})_2\text{Cl}_2$, the angle between the normals to the planes in adjacent chains is 77.89°. Consequently, to the extent that inter-chain interactions are significant (vide infra) there is an important structural distinction between the two complexes.

RESULTS AND DISCUSSION

The compounds $\text{Cu}(\text{tz})_2\text{Cl}_2$ and $\text{Cu}(\text{tz})_2\text{Br}_2$ exhibited very broad, weak symmetrical bands centered at 14,400 and 14,300 cm^{-1} , respectively; furthermore, the shape and width of these d-d bands were noted to be very similar to those observed for $\text{Cu}(\text{py})_2\text{Cl}_2$ (14,600 cm^{-1}) and $\text{Cu}(\text{py})_2\text{Br}_2$ (14,600 cm^{-1})⁴³ except for a slight shift to lower energy; this shift seems reasonable since it is known that thiazole is a weaker base than pyridine.³⁰ In addition, there were no transitions in the region 16 - 17,000 cm^{-1} as have been observed⁴³ for the $\text{Cu}(\text{2-methylpyridine})_2\text{X}_2$ compounds,⁴⁴ which are known to contain copper ions in a distorted square-based pyramidal array. Several intense higher energy bands were also observed for both complexes, these being centered at about 32,250 (strong) and 41,700 cm^{-1} for $\text{Cu}(\text{tz})_2\text{Cl}_2$ and 23,250 (strong) 31,250 (strong), 32,000 (shoulder) and 41,700 cm^{-1} for $\text{Cu}(\text{tz})_2\text{Br}_2$. These bands are either charge-transfer or intra-ligand transitions.⁴⁵ The observed electronic spectra are consistent with a distorted octahedral CuN_2X_4 chromophore as reported in extensive studies of the substituted pyridine copper halide complexes.⁴³

Electron paramagnetic resonance (epr) spectra were obtained on finely-ground polycrystalline samples of both complexes. A single broad (~300 G) featureless line centered at $g \approx 2.11$ was observed for $\text{Cu}(\text{tz})_2\text{Br}_2$; no appreciable temperature dependence was noted for this absorption down to -77°K (the low temperature limit of this investigation). Although virtually no quantitative information could be obtained from these spectra, it should be noted that qualitatively similar spectra have been observed in the bis(subst. pyridine) complexes with copper bromide.²⁸ However, the epr spectrum obtained for $\text{Cu}(\text{tz})_2\text{Cl}_2$

(see Figure 3) is quite different from that normally seen for tetragonally distorted octahedral copper complexes. Indeed, an axial "reversed" spectrum was observed with g_{\parallel} (2.16) greater than g_{\perp} (2.04) and $\langle g \rangle = 2.11$. Upon cooling the sample, the intensity of the highest field resonance increased slightly. The resonance fields remained constant within experimental error.

Since powder EPR spectra can only yield information about the values of the crystal g-tensors,⁴⁷ additional analyses based on the molecular structure must be invoked to understand the observed "reversed" spectrum. One possibility is that the single ion electronic ground state about the copper(II) ions is largely d_{z^2} .^{46,47} If only discrete molecular units are considered, several stereochemistries have been shown to give rise to a species with a d_{z^2} ground state:⁴⁷ (i) trigonal bipyramidal, (ii) tetragonally compressed octahedral, (iii) cis-distorted octahedral, and (iv) rhombically distorted octahedral. However, the X-ray structural results show that these stereochemistries do not obtain for $\text{Cu}(\text{tz})\text{Cl}_2$. In this case, it is far more likely that the single ion ground state is largely $d_{x^2-y^2}$ in character, and the observed resonance is determined by inequivalent sites within the unit cell.^{48,55-57} Since the two sites within the unit cell are magnetically inequivalent in the ac-plane, the relative orientations of the tetragonally elongated octahedra will determine the observed crystal g-tensors. Even though these molecular sites do not possess tetragonal site-symmetry, this approximation allows for a much simpler relationship of the site g-tensors to the observed powder g-tensors. These

expressions are given by (2)

$$g'_{||}^2 = g_{\perp}^2 \quad (2)$$

$$g'_{\perp}^2 = g_{\perp}^2 \cos^2 \alpha + g_{||}^2 \sin^2 \alpha$$

where $g'_{||}$ and g'_{\perp} are the observed crystal g-tensors, $g_{||}$ and g_{\perp} are the site g-tensors for the tetragonally elongated octahedra about the copper(II) ions, and 2α is the angle between the tetragonal axes of the sites. If one assumes that molecular $g_{||}$ is roughly normal to the plane of the four short bonds,^{13,14} then the angle between the normals to these two sites is 77.89° for $\text{Cu}(\text{tz})_2\text{Cl}_2$. Using this value of 2α and Equation (2), the values of the molecular g-tensors are $g_{||} = 2.23$ and $g_{\perp} = 2.04$. These values are in excellent agreement with those of the structurally similar $\text{Cu}(\text{pyridine})_2\text{Cl}_2$ complex.^{13,14} In another rather similar system, $\beta\text{-Cu}(\text{NH}_3)_2\text{Cl}_2$ doped into the NH_4Cl host lattice, Tomlinson, et al.,⁵⁰ observed a "reversed" powder spectrum with $g'_{||} = 2.006$ and $g'_{\perp} = 2.175$ and proposed that the geometry about copper was tetragonally compressed octahedral thus yielding a d_z^2 ground state. However, it is also of interest to note that this cubic cell requires the molecular tetragonal axes to be oriented randomly, but any pair of axes are exactly 90° apart. Thus, such a system will always show a "reversed" powder spectrum irrespective of whether the sites are tetragonally elongated or compressed. This unusual circumstance arises because the 90° misalignment of the molecular

parallel g-tensors yields a unique perpendicular resonance (occurring at higher field) and a lower-field, more intense resonance which is the average of the molecular parallel and perpendicular g-tensors.

The experimental magnetic susceptibilities versus absolute temperature for both complexes are plotted in Figures 4, 5, and 6. The data for the chloride complex are seen to exhibit a broad maximum at about 7°K, while the bromide analogue displays similar behavior at ca. 19°K. As can be seen from closer examination of the experimental data, the susceptibilities of both compounds appear to tend toward a non-zero value as the temperatures approach zero; this is just the behavior expected for an infinite linear chain since it is well known that, in small clusters containing even multiples of $S = 1/2$, the susceptibility tends to zero as the temperature tends to zero (see ref. 8). Also, inspection of the observed data [especially those of $\text{Cu}(\text{tz})_2\text{Br}_2$] reveals a small Curie-like tail at the very lowest temperatures; phenomena similar to these have often been observed in similar systems^{28,51} and have been attributed to the presence of small amounts of monomeric impurities (usually less than 1%) that become trapped in the material during synthetic procedures. Since these compounds are quite insoluble in all but strongly coordinating solvents (DMF), it was not possible to completely remove these impurities.

In the light of the observed crystal structure of $\text{Cu}(\text{tz})_2\text{Cl}_2$ and the similarity of the observed electronic spectra of $\text{Cu}(\text{tz})_2\text{X}_2$ with those of $\text{Cu}(\text{py})_2\text{X}_2$, it is apparent that the magnetic data of the two systems should be comparable. As was noted in the Introduction, in the Ising limit (i.e., $b = 0$ in Equation 1), Fisher⁶ has obtained closed-form expressions for the susceptibility of a $S = 1/2$ linear

chain polymer. Although these equations are readily manipulated during fitting procedures, it has been generally accepted⁵² that the totally anisotropic model is not appropriate for copper(II) ions. Furthermore, attempts to fit the data for the $\text{Cu}(\text{tz})_2\text{X}_2$ complexes with this model resulted in unacceptable parameters and rather poor agreement between the observed and calculated susceptibilities.

DeJong and Miedema¹ have suggested that the isotropic Heisenberg model (Equation 1, $a=b=1$) is probably more appropriate for systems with small g-tensor anisotropy. Although there are no closed-form solutions known for the linear Heisenberg model, there are two approximations which can be used to estimate the exchange interaction from susceptibility data. Bonner and Fisher⁸ have shown that the position of the maximum in the antiferromagnetic susceptibility can be estimated by the relationships $kT_{\text{max}}/|J| \approx 1.282$ and $|J|\chi_{\text{max}}/g^2\beta^2N \approx 0.0735$. Furthermore, Hall, *et al.*⁵³ have recently been able to fit the Bonner-Fisher curve to the following rational function of $|J|/kT$:

$$\chi \approx \frac{Ng^2\beta^2}{kT} \frac{(0.25 + 0.14995X + 0.30094 X^2)}{(1.0 + 1.9862 X + 0.68854 X^2 + 6.0626X^3)} \quad (3)$$

where

$$X = |J|/kT$$

The general form of Equation 2 has been verified by comparing the susceptibilities thus calculated with those obtained from the high-temperature series expansion (HTS) of Baker *et al.*^{10a}:

$$\frac{\chi kT}{4Ng^2\beta^2} \approx [(1.0 + 5.97979916K + 16.902653K^2 + 29.376885K^3 + 29.832959K^4 + 14.036918K^5) \div (1.0 + 2.7989916K + 7.008678K^2 + 8.0538644K^3 + 4.5743114K^4)]^{2/3} \quad (4)$$

where

$$K = \frac{J}{2kT}$$

The above series has been normalized to the Curie Law for $J = 0$ (i.e.

$\chi = \frac{Ng^2\beta^2 S(S+1)}{3kT}$ since Baker, et al.^{10a} did not include the factor of four (i.e. $S(S+1)/3$) in the denominator. In the temperature range of $kT/|J| > 1.25$, agreement between susceptibilities calculated by Equations 2 and 3 was excellent, with all disparities being less than 1%.

In view of the probable presence of impurities at temperatures low compared to T_{\max} , it was reasoned that the fitting the data to the result of Baker, et al.¹⁰ would be the most acceptable initial attempt. This is reasonable because at χ_{\max} and above the presence of the impurity can be neglected. In order to fit the data to Equation 3, $|J|$ was estimated from the corresponding temperature using Bonner and Fisher's relations and the experimental data below $kT/J = 1.25$ were omitted (i.e., those below 7° and 18°K for the chloride and bromide, respectively). The best fits of the data to Equation 3 were $\langle g \rangle = 2.06$, $J = 3.7 \text{ cm}^{-1}$ and $\langle g \rangle = 2.11$, $J = -10.3 \text{ cm}^{-1}$ for the chloride and bromide complexes, respectively (See Table 1).

To gain more information about the low-temperature behavior of the data ($kT/J \leq 1.25$), we have compared it to the results of Bonner and Fisher (Equation 3). In making this comparison, the presence of

monomeric impurities was allowed for by assuming that $\chi_{\text{obs}} = \chi_{\text{chain}} + \chi_{\text{impurity}}$. Furthermore, by assuming that the impurity obeys the Curie Law, the following expression for the total susceptibility results:⁵⁴

$$\chi_{\text{obs}} = \left\{ \frac{P[Ng^2\beta^2S(S+1)]}{3kT} + (100-P)\chi_{\text{chain}} \right\} / 100 \quad (5)$$

where $S = 1/2$, $P = \% \text{ impurity}$ and $g = \text{observed average } g\text{-value}$ from the epr spectra. For the fit using the approximation of the Bonner-Fisher curve, J and P were allowed to vary in the fitting routine. The best fits obtained in this manner were $J = -10.3\text{cm}^{-1}$, $P = 0.65\%$, and $J = -3.97\text{cm}^{-1}$, $P = 1.46\%$ for the bromide and chloride complexes, respectively (see Figures 4 and 5). In order to check the validity of the impurity correction, the next fits were performed by allowing g , J , and P to vary simultaneously; this resulted in $J = -10.4\text{cm}^{-1}$, $g = 2.12$ and $P = 0.66\%$ for $\text{Cu}(\text{tz})_2\text{Br}_2$, and $J = -3.81\text{cm}^{-1}$, and $g = 2.06$ and $P = 1.35\%$ for $\text{Cu}(\text{tz})_2\text{Cl}_2$. These fits are shown in Figures 4 and 5. Although both of the linear models appear to provide an excellent description of the susceptibility data of $\text{Cu}(\text{tz})_2\text{Br}_2$, the validity of this approach for $\text{Cu}(\text{tz})_2\text{Cl}_2$ may be in question since there are large differences in the exchange constants between $\text{Cu}(\text{tz})_2\text{X}_2$ and $\text{Cu}(\text{py})_2\text{X}_2$ while the structural details for the two compounds are very similar. Since the magnitude of the maximum in the antiferromagnetic susceptibility

is determined by the g-value for a given J, a discrepancy in this portion of the fit may imply that the model chosen is inappropriate. Thus, as the dimensionality of the magnetic interaction increases the position of the maximum in reduced coordinates becomes lower and broader.¹

The similarity of the structures of $\text{Cu}(\text{tz})_2\text{Cl}_2$ and $\text{Cu}(\text{py})_2\text{Cl}_2$ and the relatively large differences in the exchange constants for the one-dimensional analyses suggest that the magnetic interactions in the thiazole complexes are of higher dimensionality. Hence, the magnetic susceptibility data were compared to the Bonner-Fisher theory assuming a first order molecular field correction to account for interchain interactions⁵⁹ (Equation 6)

$$\chi = \frac{\chi_{\text{B-F}}}{1 - 2zJ' \frac{\chi_{\text{B-F}}}{Ng^2\beta^2}} \quad (6)$$

where $\chi_{\text{B-F}}$ is the susceptibility of an isolated Heisenberg chain, J' is the interchain exchange, and z is the number of nearest neighbors. In the calculations the g-value was fixed to that observed by EPR and J and zJ' were allowed to vary freely. This approach led to best fit values of $J = -3.31 \text{ cm}^{-1}$, $J'(Z=4) = 1.55 \text{ cm}^{-1}$ and $\langle g \rangle = 2.11$ for $\text{Cu}(\text{tz})_2\text{Cl}_2$ while the data for the bromo compound yielded $J = -10.48 \text{ cm}^{-1}$, $zJ' = +1.14 \text{ cm}^{-1}$, and $\langle g \rangle = 2.11$. Although this modified one-dimensional model makes a crude approximation to the interchain interactions present, it fails to describe the susceptibility of $\text{Cu}(\text{tz})_2\text{Cl}_2$ near the maximum since deviations of about 5% between the observed and calculated susceptibilities occur. Furthermore, the sum of the squares of the deviations of a point

from the calculated curve, $SD = \sum \left[\frac{\chi_o - \chi_{calc}}{\chi_o} \right]^2$, is 1.81×10^{-2} . The fit of

the data for the bromo compound is hardly affected by the interchain term. The failure of the molecular field approach for $\text{Cu}(\text{tz})_2\text{Cl}_2$ was not totally unexpected since molecular field theory is a very poor model for low-dimensional systems.¹

To investigate the possibility that the magnetic interactions in $\text{Cu}(\text{tz})_2\text{Cl}_2$ were of higher dimensionality, the data were fitted to the high-temperature series expansion for the two dimensional Heisenberg antiferromagnetic layer,^{10b,58}

$$\chi_{2D} = \frac{Ng^2\beta^2}{4k} \left[1 - 2(J/kT) + 2\left(\frac{J}{kT}\right)^2 + \dots \right] \quad (7)$$

Although an argument based solely on the metal-metal distances and strongly bonded ligands would imply that a 2-D planar model with four nearest neighbors should not be appropriate for this compound, inspection of the unit cell reveals that a superexchange pathway via the short sulfur-sulfur contacts does exist in the ac-plane. Furthermore, an excellent fit over the range $\frac{kT}{|J|} \geq 1.6$ can be obtained using equation (7). This leads to a best fit value of $J = -2.43 \text{ cm}^{-1}$ (see Figure 6) when only J is varied and the experimentally determined g -value from EPR, $g = 2.11$, is used. The criterion of the fit, $\left[\frac{\chi_o - \chi_{calc}}{\chi_o} \right]^2 = 2.28 \times 10^{-4}$, is three orders of magnitude better than that found for the molecular-field model fit. Attempts to fit the data for $\text{Cu}(\text{tz})_2\text{Br}_2$ to the 2-D series were unsuccessful and led to deviations as high as 8% from the calculated curve near the maximum.

The magnetic and structural properties of the $\text{Cu}(\text{tz})_2\text{X}_2$ systems are compared in Table I with those previously observed for their substituted pyridine analogues. The magnitude of the exchange, $|J|$, for both of the thiazole compounds is considerably smaller than those reported

for the $\text{Cu(py)}_2\text{X}_2$ compounds if one takes the values determined from the linear chain models. This is surprising in view of the similarity between the structure of $\text{Cu(tz)}_2\text{Cl}_2$ and $\text{Cu(py)}_2\text{Cl}_2$; in the former, the Cu-Cl-Cu' bridge angle and Cu-Cl out-of-plane distance are $91.89 (2)^\circ$ and $2.998 (1) \text{ \AA}$, respectively, while the analogous values in $\text{Cu(py)}_2\text{Cl}_2$ are $91.52 (5)^\circ$ and $3.026 (2) \text{ \AA}$. The observation may be the result of a much larger interchain exchange for the thiazole complexes since the 2-D model can be used to approximate the data of $\text{Cu(tz)}_2\text{Cl}_2$. Presumably, the additional superexchange pathway via sulfur-sulfur contacts between chains plays a very important role in this dimensionality increase.

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TABLE I

COMPLEX	$J(\text{cm}^{-1})$	$\text{Cu-X-Cu}(\text{°})$	$\text{Cu-Cu}(\text{Å})$	COMMENTS AND REFERENCE
$\text{Cu}(\text{thiazole})_2\text{Cl}_2$	-3.69	92°	3.85	1-D Series
$\text{Cu}(\text{thiazole})_2\text{Cl}_2$	-3.8	92°	3.85	Bonner-Fisher
$\text{Cu}(\text{thiazole})_2\text{Cl}_2$	-2.43	92	3.85	2-D Series
$\text{Cu}(4\text{-Ethylpyridine})_2\text{Cl}_2$	-6.7	92°	4.00	28,27a
$\text{Cu}(4\text{-Vinylpyridine})_2\text{Cl}_2$	-9.1	90°	4.04	28,27b
$\text{Cu}(\text{Pyridine})_2\text{Cl}_2$	-9.2	92°	3.87	15,23,13,24
$\text{Cu}(3\text{-Methylpyridine})_2\text{Cl}_2$	-8.9	-	-	28
$\text{Cu}(3\text{-ethylpyridine})_2\text{Cl}_2$	-11.9	-	-	28
$\text{Cu}(\text{thiazole})_2\text{Br}_2$	-10.03	-	-	1-D Series
$\text{Cu}(\text{thiazole})_2\text{Br}_2$	-10.4	-	-	Bonner-Fisher
$\text{Cu}(4\text{-Methylpyridine})_2\text{Br}_2$	-14.8	-	-	28
$\text{Cu}(4\text{-Ethylpyridine})_2\text{Br}_2$	-15.4	-	-	28
$\text{Cu}(3\text{-Methylpy})_2\text{Br}_2$	-15.5	-	-	28
$\text{Cu}(\text{Py})_2\text{Br}_2$	-18.9	93	-	15,24
$\text{Cu}(3\text{-Etpy})_2\text{Br}_2$	-22.3	-	-	28

Table II. Positional Parameters for $[\text{Cu}(\text{thz})_2\text{Cl}_2]$

	X	Y	Z
CU	0.0	0.0	0.0
CL	0.2023 (1)	0.3789 (2)	0.0546 (1)
S	-0.4279 (1)	0.0578 (2)	0.1697 (1)
N	-0.1567 (3)	0.0037 (5)	0.0888 (1)
C1	-0.3271 (3)	0.0998 (7)	0.0857 (1)
C2	-0.2286 (3)	-0.0916 (7)	0.2126 (1)
C3	-0.0990 (3)	-0.1038 (7)	0.1607 (1)
HC1	-0.383 (3)	0.167 (9)	0.042 (2)
HC2	-0.225 (4)	-0.149 (9)	0.256 (2)
HC3	0.019 (5)	-0.174 (10)	0.167 (2)

Table III. Thermal Parameters (Uij) (Å²) for [Cu(thz)₂Cl₂]

	U ₁₁ (orU) ^a	U ₂₂	U ₂₃	U ₁₂	U ₁₃	U ₂₃
C1	0.0245 (2)	0.0337 (2)	0.0205 (2)	-0.0064 (2)	0.0076 (1)	-0.0068 (2)
C2	0.0274 (2)	0.0279 (3)	0.0264 (2)	-0.0022 (2)	0.0021 (2)	-0.0033 (2)
C3	0.0287 (3)	0.0369 (3)	0.0300 (3)	0.0029 (2)	0.0118 (2)	0.0002 (2)
N1	0.0244 (8)	0.0284 (10)	0.0212 (8)	-0.0017 (7)	0.0056 (6)	-0.0035 (7)
C1	0.0276 (10)	0.0306 (12)	0.0232 (10)	0.0002 (9)	0.0045 (8)	0.0007 (9)
C2	0.0332 (11)	0.0286 (12)	0.0215 (10)	-0.0012 (9)	0.0034 (8)	0.0029 (8)
C3	0.0267 (10)	0.0302 (12)	0.0266 (10)	0.0015 (9)	0.0021 (8)	-0.0000 (9)
HC1	0.017 (8)					
HC2	0.013 (7)					
HC3	0.023 (8)					

^a The form of the anisotropic thermal ellipsoid is

$$\exp[-2\pi^2(C1_1^2 h^2 a^{*2} + U_{22}^2 k^2 b^{*2} + U_{33}^2 l^2 c^{*2} + 2U_{12} hka^*b^* + 2U_{13} hla^*c^* + 2U_{23} klb^*c^*)].$$

Table IV

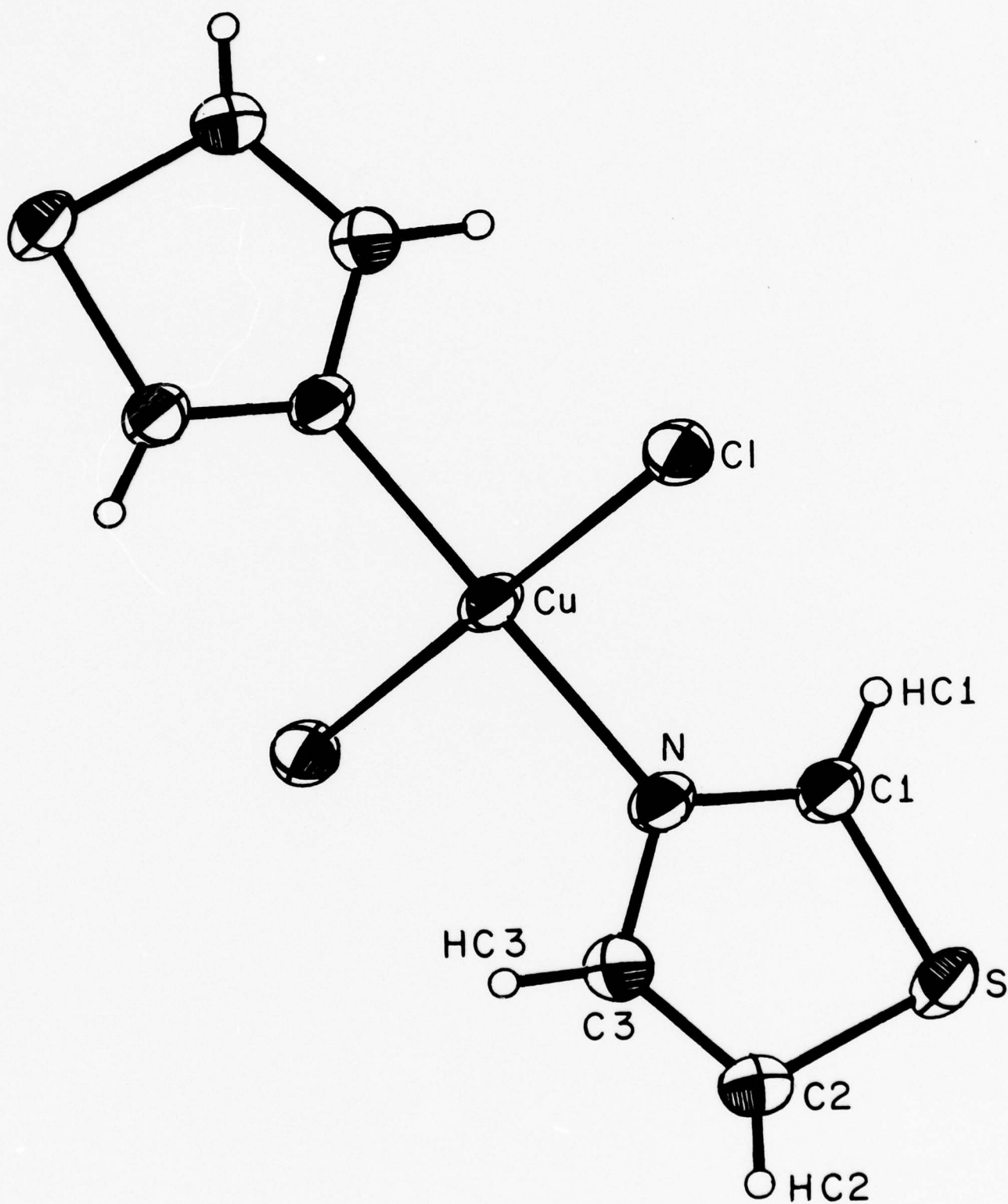
Distances and Angles in $\text{Cu}(\text{thiazole})_2\text{Cl}_2$

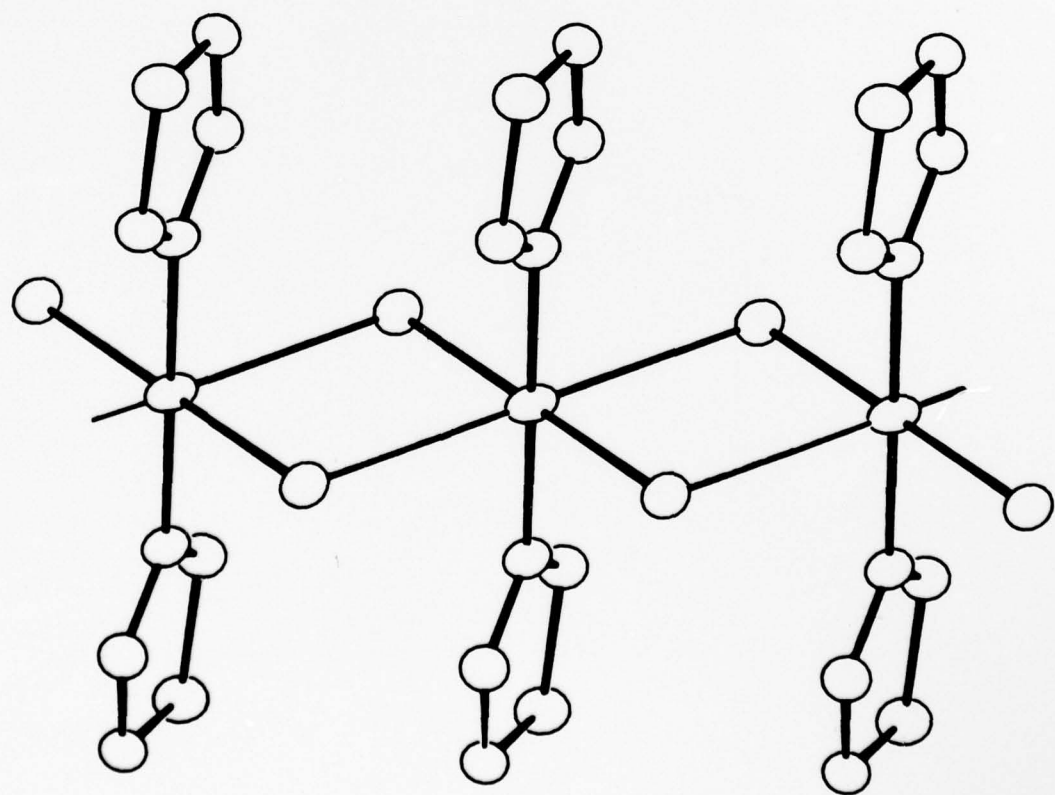
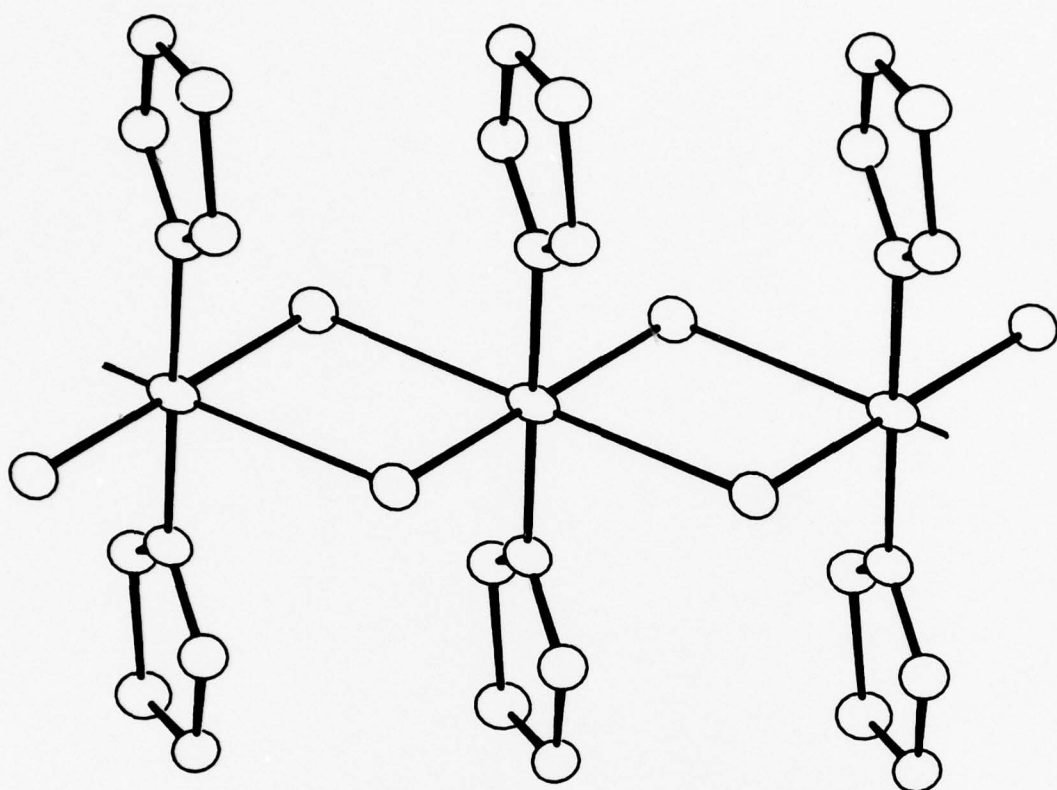
<u>Atoms</u>	<u>Distances (\AA)</u>
Cu-Cu'	3.853(4)
Cu-Cl	2.322(1)
Cu-Cl'	2.998(1)
Cu-N	1.990(2)
N-Cl	1.301(3)
N-C3	1.365(3)
S-Cl	1.694(2)
S-C2	1.700(2)
C2-C3	1.358(3)
Cl-HC1	0.877(27)
C2-HC2	0.794(30)
C3-HC3	0.906(33)
	<u>Angles (deg)</u>
Cl'-Cu-N	90.45(6)
Cl-Cu-N	89.90(6)
Cu-Cl-Cu'	91.89(2)
Cu-N-Cl	124.8(2)
Cu-N-C3	123.8(2)
Cl-N-C3	111.3(2)
N-Cl-S	113.1(2)
N-C3-C2	114.7(2)
Cl-S-C2	90.3(1)
S-C2-C3	109.5(2)
N-Cl-HC1	120.7(18)
S-Cl-HC1	125.1(17)
S-C2-HC2	119.3(22)
C3-C2-HC2	131.0(22)
N-C3-HC3	115.7(19)
C2-C3-HC3	129.6(19)

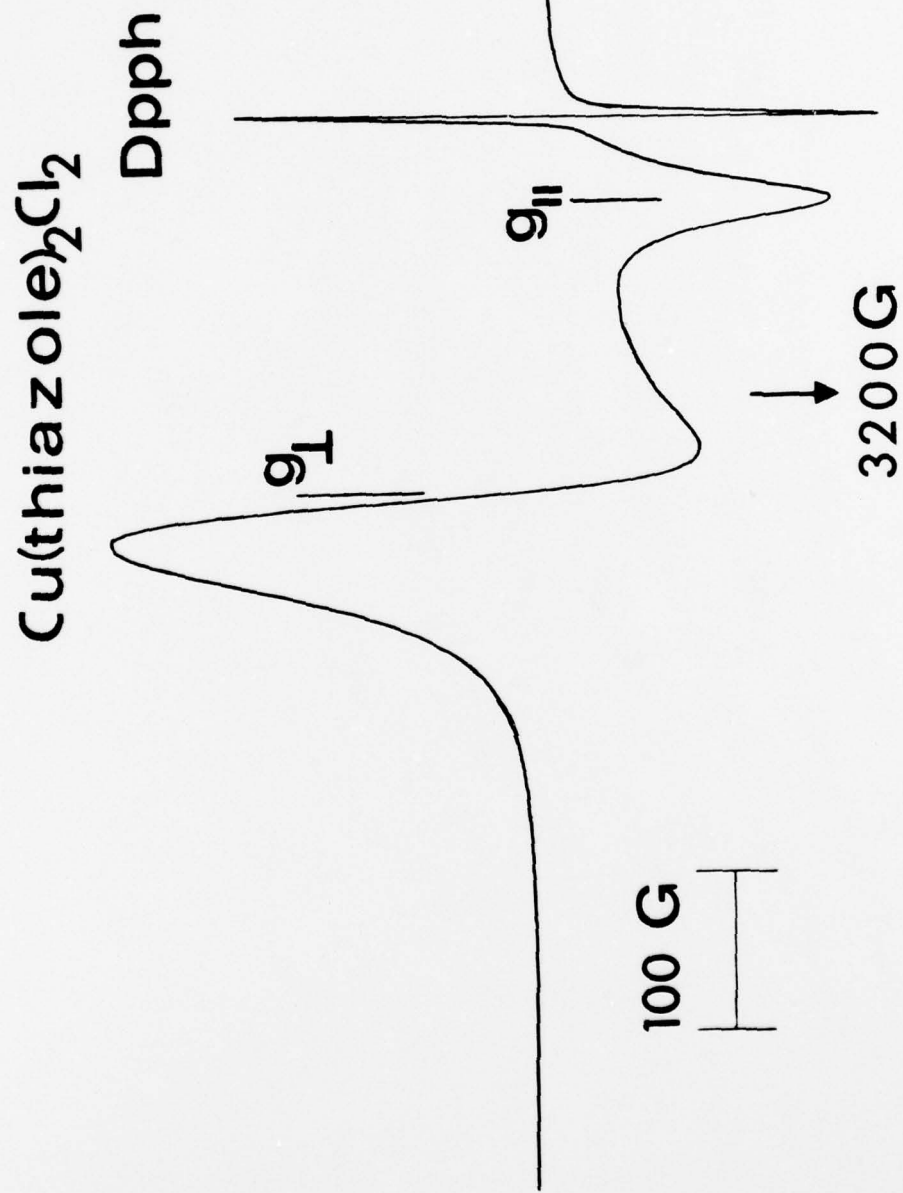
' a translation of the molecule along the b-axis

Legends for Figures

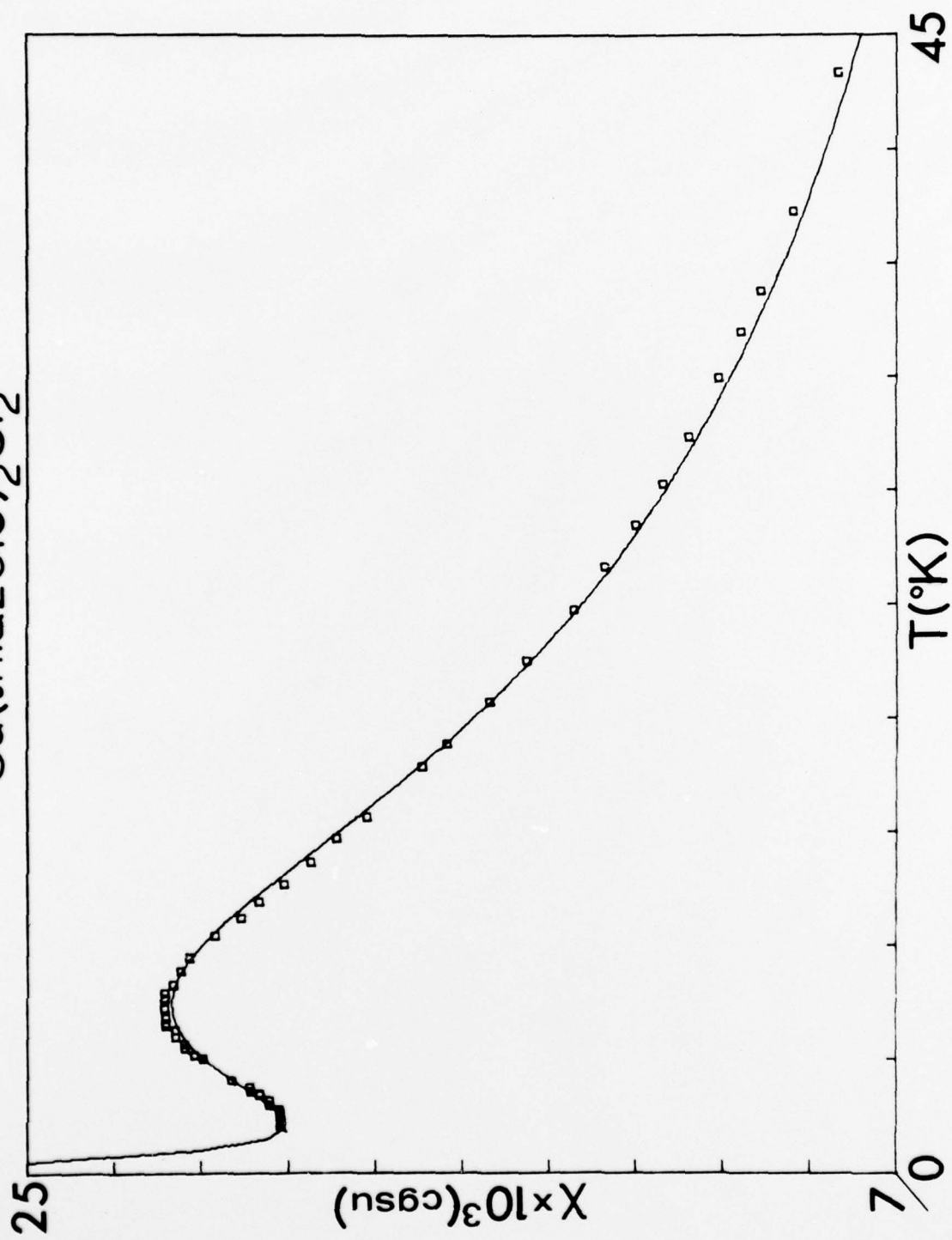
- Figure 1. View of a single formula unit of $\text{Cu}(\text{tz})_2\text{Cl}_2$. Hydrogen atoms are shown as open circles of arbitrary size. The view direction is parallel to the crystallographic b -axis.
- Figure 2. View of the chain structure in $\text{Cu}(\text{tz})_2\text{Cl}_2$. The view direction is parallel to the crystallographic a^* -axis.
- Figure 3. The room temperature epr spectrum (X-band) of polycrystalline $\text{Cu}(\text{tz})_2\text{Cl}_2$. The resonance fields show no temperature dependence down to 77°K.
- Figure 4. The temperature dependence of the magnetic susceptibility of $\text{Cu}(\text{tz})_2\text{Cl}_2$. The observed data are shown as boxes, while the solid line represents the best fit to the Bonner and Fisher expression (see text) with $J = -3.81 \text{ cm}^{-1}$ and $g = 2.06$.
- Figure 5. The temperature dependence of the magnetic susceptibility of $\text{Cu}(\text{tz})_2\text{Br}_2$. The solid line represents the best fit to the Bonner and Fisher expression (see text) with $J = 10.4 \text{ cm}^{-1}$ and $g = 2.12$.
- Figure 6. The high temperature susceptibility, $\frac{kT}{|J|} \geq 1.6$, compared to the theoretical model of a two dimensional Heisenberg layer (see text) with $J = -2.43$, $g = 2.11$.



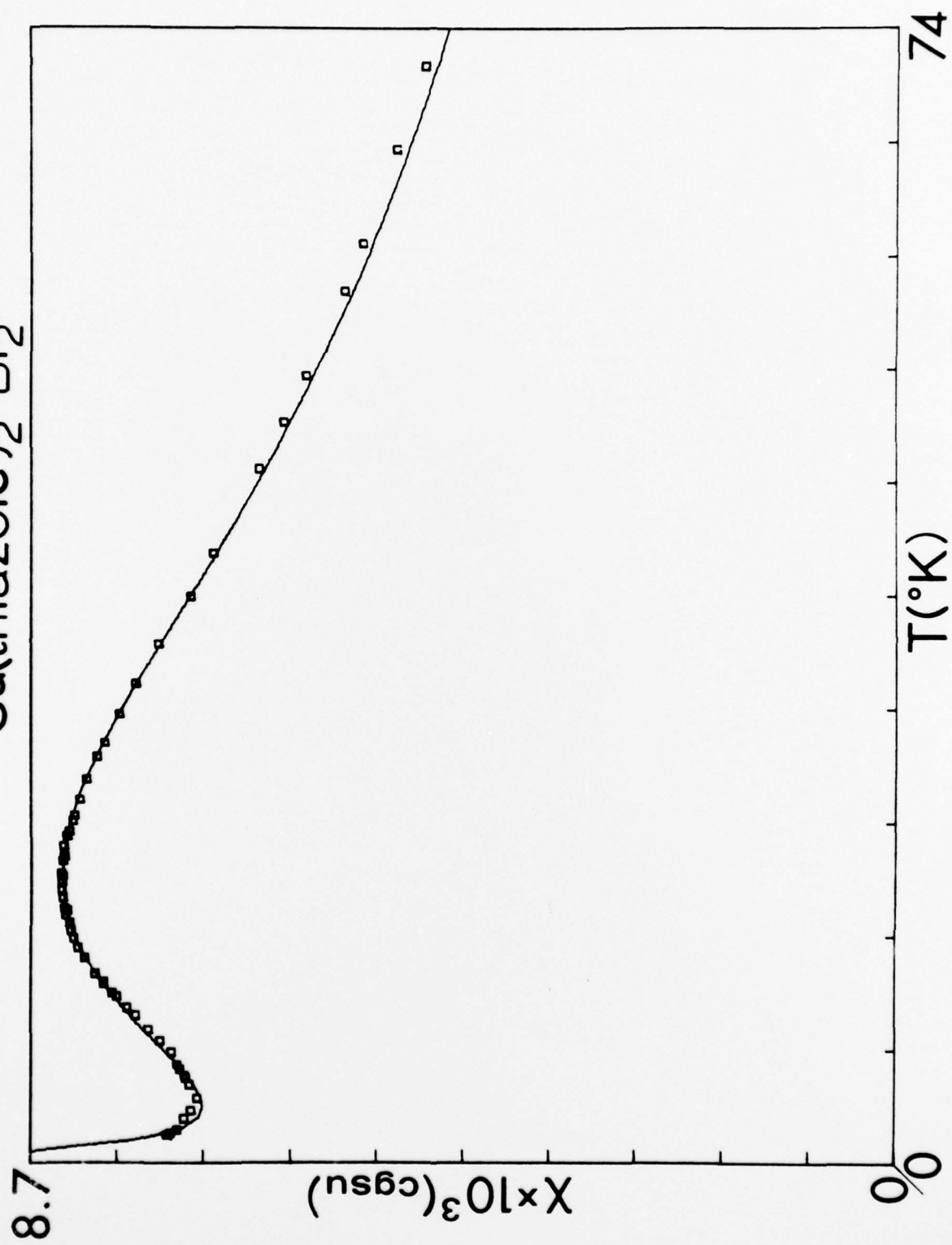


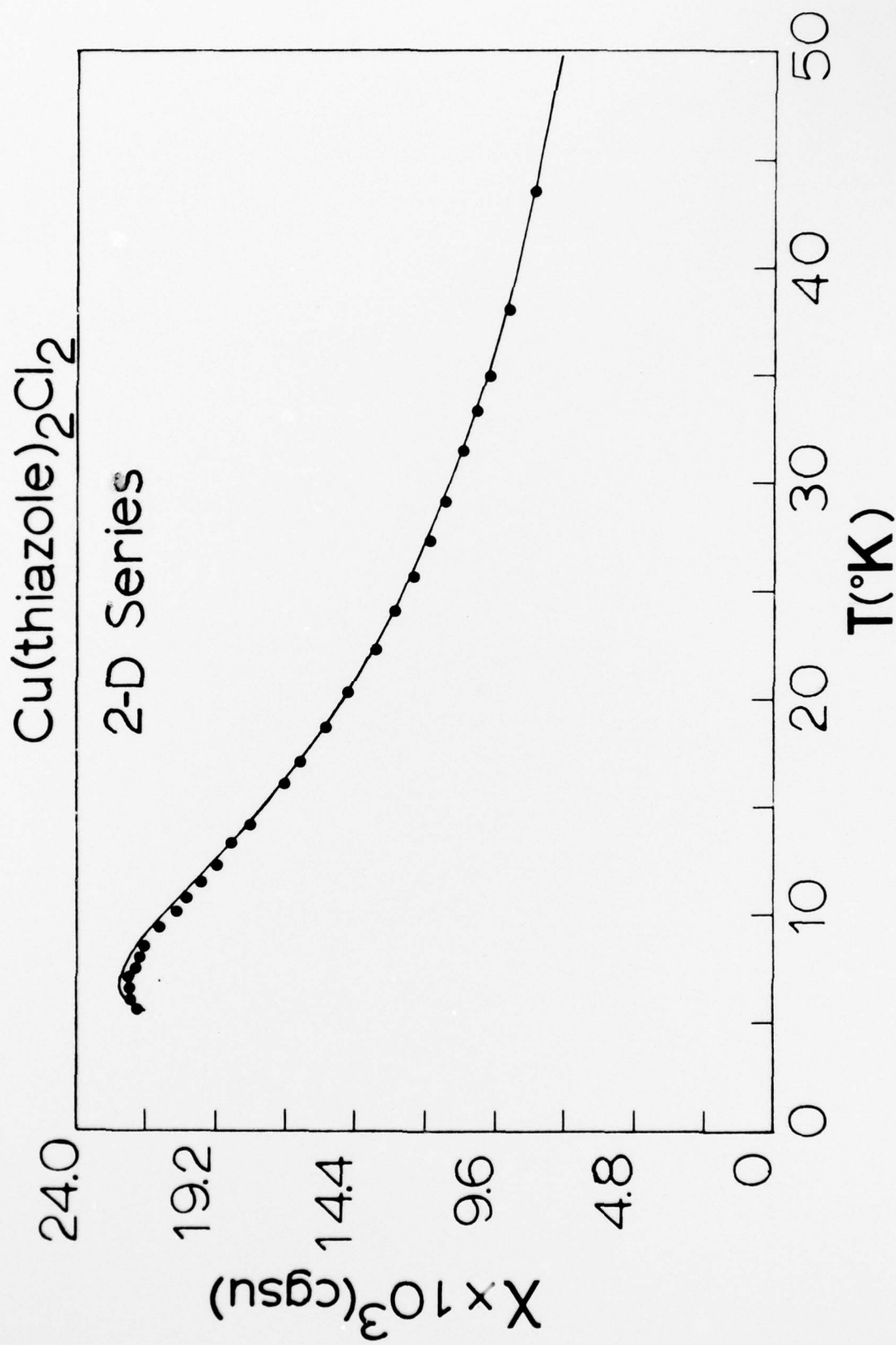


$\text{Cu}(\text{thiazole})_2\text{Cl}_2$



$\text{Cu}(\text{thiazole})_2 \text{Br}_2$





Supplementary material available: Listings of structure factor amplitudes
(7 pages). Ordering information is given on the current masthead page.

H	K	L	FO	PC	H	K	L	FO	PC	H	K	L	FO	PC
0	0	2	573	595	0	3	10	296	298	1	1	-10	190	186
0	0	4	42	45	0	3	11	223	221	1	1	-9	927	942
0	0	6	321	330	0	3	12	86	87	1	1	-8	60	60
0	0	8	389	362	0	3	13	226	228	1	1	-7	251	257
0	0	10	183	175	0	3	15	152	154	1	1	-6	219	219
0	0	12	739	758	0	3	16	80	78	1	1	-5	51	53
0	0	14	372	371	0	3	17	176	177	1	1	-4	182	174
0	0	16	208	206	0	3	18	102	102	1	1	-3	196	203
0	0	18	375	376	0	3	19	81	78	1	1	-2	305	289
0	1	1	839	796	0	4	0	62	58	1	1	-1	427	391
0	1	2	397	363	0	4	1	78	77	1	1	0	357	328
0	1	3	365	328	0	4	2	52	54	1	1	1	973	962
0	1	4	462	428	0	4	4	125	123	1	1	2	103	95
0	1	5	695	697	0	4	5	106	107	1	1	3	1148	1138
0	1	6	162	155	0	4	6	208	212	1	1	4	334	310
0	1	7	579	595	0	4	7	60	53	1	1	5	528	507
0	1	8	23	17	0	4	8	252	255	1	1	6	167	159
0	1	9	315	321	0	4	10	191	191	1	1	7	489	492
0	1	10	297	308	0	4	11	87	89	1	1	8	333	316
0	1	11	641	640	0	4	12	94	89	1	1	9	300	318
0	1	12	143	141	0	4	13	96	96	1	1	10	62	68
0	1	13	339	343	0	5	1	124	124	1	1	11	70	75
0	1	14	43	43	0	5	3	142	149	1	1	12	116	116
0	1	15	144	151	0	5	4	119	120	1	1	13	192	195
0	1	17	71	73	1	0	-24	54	53	1	1	14	34	43
0	1	18	126	129	1	0	-20	351	349	1	1	15	335	338
0	1	19	164	170	1	0	-18	303	302	1	1	16	155	155
0	1	20	42	43	1	0	-16	306	313	1	1	18	84	86
0	1	21	76	78	1	0	-14	151	143	1	1	19	252	251
0	1	23	300	293	1	0	-12	140	138	1	1	21	216	217
0	2	0	882	828	1	0	-10	346	343	1	1	22	57	55
0	2	1	104	91	1	0	-8	548	565	1	1	23	49	40
0	2	2	282	268	1	0	-6	240	246	1	2	-22	173	167
0	2	3	192	184	1	0	-4	1156	1242	1	2	-21	71	69
0	2	4	173	168	1	0	-2	471	484	1	2	-20	186	183
0	2	5	386	370	1	0	0	464	475	1	2	-19	163	160
0	2	6	410	401	1	0	2	1007	1147	1	2	-18	82	82
0	2	7	39	30	1	0	4	92	79	1	2	-17	178	179
0	2	8	120	117	1	0	6	120	115	1	2	-16	163	169
0	2	9	34	28	1	0	8	361	382	1	2	-15	94	96
0	2	10	270	261	1	0	10	373	386	1	2	-14	166	164
0	2	11	100	96	1	0	12	453	440	1	2	-13	31	25
0	2	12	415	416	1	0	14	721	740	1	2	-12	83	85
0	2	13	307	309	1	0	16	201	197	1	2	-11	238	240
0	2	14	134	132	1	0	18	89	98	1	2	-10	422	423
0	2	16	77	79	1	0	20	106	111	1	2	-9	237	238
0	2	17	92	99	1	0	22	70	69	1	2	-8	437	424
0	2	18	198	200	1	0	24	100	93	1	2	-7	480	465
0	2	19	116	112	1	1	-23	102	103	1	2	-6	88	91
0	2	20	67	68	1	1	-22	134	133	1	2	-5	151	141
0	2	21	167	169	1	1	-21	203	200	1	2	-4	453	438
0	2	22	115	111	1	1	-19	47	44	1	2	-2	274	270
0	3	1	474	444	1	1	-18	47	49	1	2	-1	86	80
0	3	2	272	258	1	1	-17	47	48	1	2	0	237	225
0	3	3	211	201	1	1	-15	52	58	1	2	1	737	700
0	3	4	141	132	1	1	-15	222	226	1	2	2	757	689
0	3	5	135	132	1	1	-14	286	288	1	2	3	280	258
0	3	6	71	74	1	1	-13	239	235	1	2	4	357	330
0	3	7	58	60	1	1	-12	28	21	1	2	5	324	300
0	3	8	49	50	1	1	-11	482	487	1	2	6	105	97

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	2	7	42	38	1	4	2	235	229	2	1	3	561	549
1	2	8	303	307	1	4	4	310	303	2	1	4	485	473
1	2	9	338	334	1	4	5	88	87	2	1	5	727	724
1	2	10	199	201	1	4	6	160	153	2	1	6	97	98
1	2	11	124	120	1	4	7	121	120	2	1	7	229	218
1	2	12	153	151	1	4	8	142	136	2	1	8	183	180
1	2	13	220	219	1	4	9	69	67	2	1	9	148	135
1	2	14	362	362	1	4	10	52	55	2	1	11	260	268
1	2	15	136	139	1	4	13	92	95	2	1	12	236	236
1	2	16	147	145	1	5	-8	114	111	2	1	13	125	123
1	2	17	109	111	1	5	-7	78	68	2	1	14	78	82
1	2	18	41	37	1	5	-5	91	93	2	1	15	253	257
1	2	19	74	68	1	5	-3	129	132	2	1	17	402	403
1	2	20	148	150	1	5	-1	174	177	2	1	19	125	121
1	2	22	45	49	1	5	0	96	90	2	1	20	79	77
1	3	-20	68	62	1	5	1	50	43	2	1	21	97	99
1	3	-19	137	135	1	5	2	101	95	2	1	22	98	97
1	3	-18	69	65	1	5	4	65	50	2	1	23	59	48
1	3	-17	128	132	1	5	9	74	80	2	2	-22	42	47
1	3	-15	179	178	2	0	-24	200	197	2	2	-21	72	75
1	3	-14	278	281	2	0	-20	231	230	2	2	-20	135	133
1	3	-11	56	57	2	0	-18	405	408	2	2	-19	129	126
1	3	-10	178	173	2	0	-14	87	80	2	2	-18	248	249
1	3	-9	209	213	2	0	-12	344	346	2	2	-17	45	52
1	3	-8	34	32	2	0	-10	25	21	2	2	-16	79	76
1	3	-7	129	126	2	0	-8	760	786	2	2	-15	149	152
1	3	-6	136	139	2	0	-6	1323	1410	2	2	-14	126	126
1	3	-5	235	236	2	0	-4	386	394	2	2	-13	163	165
1	3	-4	145	140	2	0	-2	430	440	2	2	-12	308	310
1	3	-3	433	429	2	0	0	58	77	2	2	-11	316	322
1	3	-2	231	231	2	0	2	255	252	2	2	-10	84	89
1	3	-1	282	280	2	0	4	226	234	2	2	-9	91	90
1	3	0	120	120	2	0	6	875	879	2	2	-8	394	394
1	3	1	232	227	2	0	8	417	413	2	2	-7	31	26
1	3	2	98	90	2	0	10	551	570	2	2	-6	523	518
1	3	3	255	239	2	0	12	468	465	2	2	-5	26	20
1	3	4	277	258	2	0	14	41	36	2	2	-4	96	96
1	3	5	41	42	2	0	16	149	152	2	2	-3	438	429
1	3	6	126	123	2	0	22	181	180	2	2	-2	305	302
1	3	7	51	54	2	1	-21	44	48	2	2	-1	244	235
1	3	8	241	237	2	1	-19	228	230	2	2	0	377	370
1	3	9	255	257	2	1	-18	158	159	2	2	1	241	229
1	3	11	222	223	2	1	-17	334	330	2	2	2	203	189
1	3	12	163	162	2	1	-16	82	80	2	2	3	194	176
1	3	13	260	263	2	1	-15	150	151	2	2	4	438	421
1	3	15	191	192	2	1	-13	535	543	2	2	5	305	291
1	3	16	130	126	2	1	-11	322	325	2	2	6	436	412
1	3	18	51	55	2	1	-10	232	228	2	2	7	319	304
1	4	-14	126	118	2	1	-9	38	37	2	2	8	81	74
1	4	-13	79	77	2	1	-8	252	250	2	2	9	152	152
1	4	-12	184	181	2	1	-7	600	604	2	2	10	240	238
1	4	-11	100	104	2	1	-6	61	62	2	2	11	60	65
1	4	-10	266	269	2	1	-5	148	153	2	2	12	263	264
1	4	-9	60	62	2	1	-4	264	260	2	2	13	141	139
1	4	-8	172	173	2	1	-3	97	96	2	2	14	97	93
1	4	-7	102	99	2	1	-2	212	201	2	2	15	240	245
1	4	-4	53	53	2	1	-1	726	748	2	2	16	223	225
1	4	-1	67	69	2	1	0	485	470	2	2	17	41	49
1	4	0	79	78	2	1	1	653	658	2	2	18	117	115
1	4	1	169	170	2	1	2	128	124	2	2	19	134	136

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	2	22	87	88	2	5	-2	117	126	3	1	11	56	52
2	3	-20	43	29	2	5	5	74	77	3	1	12	67	70
2	3	-19	191	194	2	5	6	95	89	3	1	13	500	510
2	3	-18	155	155	2	5	7	62	47	3	1	15	274	276
2	3	-17	87	84	3	0	-24	152	149	3	1	16	77	75
2	3	-16	72	69	3	0	-22	257	255	3	1	17	100	100
2	3	-14	51	54	3	0	-20	42	35	3	1	18	149	149
2	3	-13	72	62	3	0	-18	68	74	3	1	19	128	125
2	3	-12	53	54	3	0	-16	319	316	3	2	-22	133	129
2	3	-11	96	91	3	0	-12	299	296	3	2	-20	77	78
2	3	-10	130	132	3	0	-10	899	938	3	2	-19	57	54
2	3	-9	226	228	3	0	-8	283	292	3	2	-18	91	91
2	3	-8	220	224	3	0	-6	481	479	3	2	-17	37	32
2	3	-7	437	440	3	0	-4	527	555	3	2	-16	302	306
2	3	-6	92	94	3	0	-2	309	300	3	2	-15	133	134
2	3	-5	276	279	3	0	0	113	97	3	2	-14	100	98
2	3	-4	174	177	3	0	2	832	867	3	2	-13	205	200
2	3	-3	113	115	3	0	4	416	408	3	2	-12	110	112
2	3	-1	182	183	3	0	6	598	596	3	2	-11	64	68
2	3	0	318	319	3	0	8	877	891	3	2	-10	384	390
2	3	1	53	40	3	0	10	34	36	3	2	-9	74	77
2	3	2	67	65	3	0	12	57	59	3	2	-8	145	150
2	3	3	117	115	3	0	14	172	175	3	2	-7	130	135
2	3	4	394	384	3	0	16	67	70	3	2	-6	297	298
2	3	5	323	316	3	0	18	156	157	3	2	-5	452	452
2	3	7	186	181	3	0	20	259	247	3	2	-4	499	495
2	3	8	154	151	3	0	22	141	139	3	2	-3	63	59
2	3	9	202	195	3	1	-23	78	79	3	2	-2	107	109
2	3	10	46	43	3	1	-22	79	77	3	2	-1	56	43
2	3	11	262	264	3	1	-21	181	182	3	2	0	146	147
2	3	12	199	200	3	1	-20	135	134	3	2	1	232	223
2	3	13	111	110	3	1	-19	79	81	3	2	2	456	453
2	3	15	69	65	3	1	-17	402	406	3	2	3	423	416
2	3	16	67	73	3	1	-16	66	67	3	2	4	189	186
2	3	17	73	67	3	1	-15	413	414	3	2	6	261	259
2	4	-16	99	99	3	1	-14	112	113	3	2	7	129	129
2	4	-14	178	175	3	1	-13	57	64	3	2	8	400	403
2	4	-12	135	134	3	1	-12	149	154	3	2	9	224	227
2	4	-11	101	99	3	1	-11	322	329	3	2	10	44	42
2	4	-10	129	126	3	1	-10	50	49	3	2	11	237	237
2	4	-9	60	55	3	1	-9	143	151	3	2	12	151	149
2	4	-8	66	69	3	1	-8	234	232	3	2	13	75	72
2	4	-5	94	95	3	1	-7	67	67	3	2	14	225	227
2	4	-4	41	34	3	1	-6	157	154	3	2	15	125	124
2	4	-3	97	97	3	1	-5	720	739	3	2	16	65	68
2	4	-2	106	109	3	1	-4	122	125	3	2	17	72	67
2	4	0	268	275	3	1	-3	634	666	3	2	18	110	114
2	4	1	122	121	3	1	-2	64	68	3	2	20	114	108
2	4	2	263	263	3	1	-1	286	298	3	3	-19	41	43
2	4	3	161	157	3	1	0	317	308	3	3	-17	82	82
2	4	4	289	282	3	1	1	678	699	3	3	-16	39	49
2	4	6	70	63	3	1	2	129	130	3	3	-15	108	106
2	4	7	84	83	3	1	3	476	474	3	3	-14	51	55
2	4	8	96	91	3	1	4	180	176	3	3	-13	54	57
2	4	9	95	92	3	1	5	210	200	3	3	-12	137	137
2	4	14	128	138	3	1	6	59	55	3	3	-11	196	198
2	4	15	93	94	3	1	7	365	366	3	3	-9	308	309
2	5	-7	124	125	3	1	8	128	126	3	3	-8	222	226
2	5	-5	119	120	3	1	9	212	207	3	3	-7	229	236
2	5	-3	51	48	3	1	10	135	134	3	3	-6	33	26

H	K	L	FO	PC	H	K	L	FO	PC	H	K	L	FO	PC
3	3	-5	252	256	4	0	2	354	367	4	2	-7	42	44
3	3	-4	93	97	4	0	4	981	1029	4	2	-6	251	258
3	3	-3	101	103	4	0	6	296	289	4	2	-5	120	121
3	3	-2	90	92	4	0	8	93	97	4	2	-4	190	187
3	3	-1	82	79	4	0	10	165	167	4	2	-3	31	28
3	3	0	259	262	4	0	12	176	182	4	2	-2	393	403
3	3	1	135	133	4	0	14	107	113	4	2	-1	335	338
3	3	2	38	43	4	0	16	348	354	4	2	0	155	165
3	3	3	252	250	4	0	18	221	221	4	2	1	137	138
3	3	4	96	97	4	0	20	138	140	4	2	2	77	78
3	3	5	307	302	4	0	22	128	123	4	2	3	150	154
3	3	6	128	123	4	1	-21	145	145	4	2	4	416	420
3	3	7	344	341	4	1	-19	352	349	4	2	5	134	133
3	3	8	82	82	4	1	-17	92	94	4	2	6	215	212
3	3	9	150	150	4	1	-16	97	97	4	2	7	120	122
3	3	10	92	84	4	1	-15	173	176	4	2	8	170	171
3	3	15	49	56	4	1	-14	139	135	4	2	9	243	244
3	3	17	78	86	4	1	-13	182	180	4	2	10	252	258
3	3	18	154	157	4	1	-12	114	115	4	2	12	37	34
3	4	-15	61	54	4	1	-11	96	104	4	2	13	128	126
3	4	-14	118	120	4	1	-10	66	67	4	2	14	65	69
3	4	-11	50	51	4	1	-9	289	292	4	2	16	168	171
3	4	-10	55	56	4	1	-8	88	86	4	2	17	101	106
3	4	-9	75	75	4	1	-7	572	586	4	2	18	98	96
3	4	-8	47	54	4	1	-6	295	296	4	2	20	67	71
3	4	-6	112	116	4	1	-5	447	449	4	3	-17	61	63
3	4	-5	116	116	4	1	-4	133	135	4	3	-16	68	68
3	4	-4	222	231	4	1	-3	544	551	4	3	-15	168	171
3	4	-3	80	83	4	1	-2	224	236	4	3	-14	125	126
3	4	-2	211	216	4	1	-1	445	462	4	3	-13	286	287
3	4	-1	59	57	4	1	0	158	155	4	3	-12	151	150
3	4	0	173	174	4	1	1	209	201	4	3	-11	127	124
3	4	1	53	50	4	1	2	172	176	4	3	-9	109	108
3	4	2	96	94	4	1	3	197	198	4	3	-7	156	159
3	4	3	108	107	4	1	5	360	357	4	3	-6	287	289
3	4	4	66	56	4	1	6	258	256	4	3	-4	143	145
3	4	5	58	56	4	1	7	85	83	4	3	-3	135	139
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3	4	11	64	60	4	1	9	482	494	4	3	-1	228	238
3	4	12	114	114	4	1	10	39	41	4	3	0	44	45
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3	4	14	154	148	4	1	12	37	43	4	3	2	187	187
3	5	-6	102	108	4	1	13	91	92	4	3	3	242	241
3	5	-5	47	55	4	1	14	163	167	4	3	5	289	285
3	5	-2	47	39	4	1	15	211	218	4	3	6	226	215
3	5	2	62	66	4	1	16	100	101	4	3	7	121	116
3	5	3	61	65	4	1	17	98	100	4	3	8	64	69
3	5	5	190	196	4	1	21	67	58	4	3	9	75	72
4	0	-22	80	81	4	2	-21	102	97	4	3	10	58	58
4	0	-20	114	118	4	2	-20	143	144	4	3	11	45	49
4	0	-18	120	114	4	2	-19	100	98	4	3	14	163	166
4	0	-16	104	112	4	2	-18	152	151	4	3	15	100	95
4	0	-14	554	563	4	2	-17	220	222	4	3	16	94	98
4	0	-12	359	354	4	2	-16	89	93	4	3	17	154	159
4	0	-10	268	264	4	2	-14	300	302	4	4	-14	45	46
4	0	-8	450	457	4	2	-13	56	55	4	4	-11	52	48
4	0	-6	106	105	4	2	-12	152	150	4	4	-10	56	51
4	0	-4	40	51	4	2	-10	66	67	4	4	-9	140	138
4	0	-2	385	399	4	2	-9	425	434	4	4	-8	119	117
4	0	0	285	307	4	2	-8	317	325	4	4	-7	54	60

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4	4	-6	220	225	5	1	5	261	268	5	3	7	95	97
4	4	-5	56	53	5	1	7	540	543	5	3	8	92	93
4	4	-4	229	229	5	1	8	60	59	5	3	10	118	119
4	4	-3	106	114	5	1	9	313	309	5	3	11	92	94
4	4	-2	208	215	5	1	10	131	136	5	3	12	143	149
4	4	-1	73	71	5	1	11	173	180	5	3	13	156	161
4	4	2	68	75	5	1	12	152	155	5	3	15	86	84
4	4	3	92	92	5	1	13	80	74	5	4	-12	104	110
4	4	4	47	48	5	1	15	55	56	5	4	-10	142	144
4	4	6	100	105	5	1	19	157	158	5	4	-9	56	61
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4	4	10	180	183	5	2	-16	219	218	5	4	-6	168	174
4	4	12	151	151	5	2	-15	73	77	5	4	-4	75	69
4	5	-1	52	60	5	2	-14	99	99	5	4	-3	62	59
4	5	0	90	87	5	2	-13	208	213	5	4	-1	76	69
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5	0	-18	274	268	5	2	-10	217	219	5	4	6	155	160
5	0	-16	473	471	5	2	-7	149	157	5	4	8	185	186
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5	0	-8	269	275	5	2	-3	251	261	6	0	-16	161	154
5	0	-6	146	145	5	2	-2	124	124	6	0	-14	316	317
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5	1	-7	197	197	5	3	-3	180	179	6	1	-9	454	456
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5	1	-3	240	242	5	3	1	288	294	6	1	-5	196	208
5	1	-2	154	159	5	3	2	169	172	6	1	-4	91	96
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5	1	3	56	54	5	3	5	43	28	6	1	-1	177	181
5	1	4	105	108	5	3	6	65	71	6	1	0	162	164

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6	1	5	210	210	6	3	9	159	163	7	2	-10	142	141
6	1	6	99	100	6	3	11	139	146	7	2	-9	120	122
6	1	7	88	88	6	3	12	54	54	7	2	-8	100	102
6	1	8	199	197	6	3	13	110	112	7	2	-7	50	52
6	1	9	264	264	6	4	-8	92	85	7	2	-6	232	233
6	1	10	56	57	6	4	-7	68	61	7	2	-4	43	48
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6	1	13	59	56	6	4	-1	48	31	7	2	-2	96	95
6	1	14	63	61	6	4	0	79	83	7	2	-1	263	249
6	1	15	114	112	6	4	1	53	43	7	2	0	252	253
6	1	16	84	93	6	4	2	110	111	7	2	2	120	118
6	1	17	43	52	6	4	4	155	159	7	2	3	84	74
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6	2	-12	106	109	7	0	-12	232	232	7	2	10	78	78
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6	3	1	73	74	7	1	15	79	74	8	1	-7	36	35

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H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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8	1	-5	160	159	8	2	11	52	60	9	1	-1	207	206
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8	1	-2	90	92	8	3	-7	94	95	9	1	3	48	50
8	1	-1	155	154	8	3	-5	41	42	9	1	4	44	35
8	1	0	122	126	8	3	-3	49	41	9	1	5	162	154
8	1	1	129	131	8	3	-2	110	117	9	1	6	62	58
8	1	2	117	118	8	3	0	118	121	9	1	9	74	78
8	1	3	200	201	8	3	1	82	79	9	2	-9	106	104
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8	1	13	147	150	9	0	-8	133	129	9	2	0	125	118
8	2	-13	124	126	9	0	-6	103	105	9	2	1	76	73
8	2	-10	190	186	9	0	-4	118	117	9	2	4	129	124
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8	2	8	124	119	9	1	-4	59	58	10	1	1	85	78
8	2	9	48	50	9	1	-3	72	74					

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